Treatment of sugi (*Cryptomeria japonica* D.) sapwood with aqueous solution of acetic acid

LU Bao-wang [1], DU Guang-hua [2], MATSUI Takanao [1], MATSUSHITA Yoh-ichi [1]
[1] *Graduate School of Engineering, Miyazaki University, 889-2192, Japan*
[2] *Agriculture Agency of Henan Province, Zhengzhou 450008, P. R. China*

Abstract: Sugi sapwood samples were processed with aqueous solution of acetic acid in order to find the response of the weight of sugi sapwood and the treatment of aqueous solution of acetic acid. The result showed that loss of weight for the treated sugi sapwood was about equal to yield of extracts from sugi sapwood, and increased with the increment of the concentration of aqueous solution of acetic acid. Fourier transform infrared spectroscopy spectra changes of the treated sugi wood and extracts from sugi sapwood were analyzed by FT-IR spectroscopic technique. Increasing tendency of absorption intensities of the stretching vibration at 3 400 cm^{-1} of hydroxyl group (OH) and C=C in lignin stretching vibration at 1510 cm^{-1} of benzene ring in lignin were observed from FT-IR of the treated sugi sapwood. From FT-IR spectra of extracts from sugi sapwood by aqueous solution of acetic acid, the dissolution of lignin was observed during the treatment with 30 % acetic acid solution aqueous.
Keywords: Sugi; *Cryptomeria japonica*; Sapwood; Acetic-acid aqueous solution; Fourier transform infrared spectroscopy.
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Introduction

Sugi wood (*Cryptomeria japonica* D.) is produced in large quantities in Japan. In view of the future it is our task and duty to utilize sugi wood economically because it is a significant resource for the human race. In recent years a worldwide increase of interest can be observed in the field of chemical and energetic utilization of sugi wood. Solvent extraction of chemical components and carbonization is a utilizing method for sugi wood as biomass material (Matsui T. 2000 & 2002).

Sugi wood is comprised of cellulose, hemicelluloses and lignin, which are present in all woods. Changes of sugi wood composition and properties may be caused by solution with different pH values. Moreover, there are a few reports on modification of sugi sapwood by treatment with weak acid solution. Hydrolysis of hemicelluloses in sugi wood was caused by treatment with hot spring water (weak acid solution), and property of sugi wood can be improved (Sasaki A. 1997 & 2001).

In this study, the carbonization of sugi wood and utilization of carbonization products were studied. Acetic acid is the largest components in wood and vinegar is a byproduct from carbonization of sugi wood, being about 3% (Matsui T. 2000 & 2002). Acetic acid aqueous solution was used to treat the samples of sugi wood, and the effect of treatment was investigated by Fourier transform infrared spectroscopy (FT-IR) spectra analyses.

Biography: LU Bao-wang (1967-), male, Ph. Doctor student, lecturer in Graduate School of Engineering, Miyazaki University, 889-2192, Japan.
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Materials and methods

Sugi sapwood samples used in this study were produced in Miyazaki prefecture of Japan. They were powdered in a mill, passing through 60 mesh and trapped in 115 mesh, and then dried at 100 °C for 24 h.

Acetic acid of CP grade was used. About 30 g of sugi sapwood samples were immersed in the 300-mL 0, 3%, 30% aqueous solutions of acetic acid, respectively, for about 1 h at room temperature of 25°C with a supersonic waves cleaning apparatus (Sndto). Subsequently, they were filtered through a fused glass funnel with a rotary evaporator (Techno Sigma), washed with distilled water, firstly dried at 50°C for 24 h because the moisture content of the treated sugi sapwood was high and physical change and chemical reaction may be occurred as these are directly dried at high temperature, and then at 100°C for 16 h in a drying apparatus (Tokyo Rikakikai). Moisture content of the treated samples was nearly similar to the untreated sample, being about 0.9%.

Freeze-drying of the filtrate obtained from the treatment of sugi sapwood with aqueous solution of acetic acid was carried out to obtain extracts. FT-IR spectra of the treated sugi sapwood and extracts from sugi sapwood were measured on a KBr disk, after 1-mg samples were mixed with 200-mg KBr, and rubbed to crush with a mortar. On the other hand, the extracts were extracted at room temperature about 25°C for 30 min with 20-ml distilled water under stirring, filtered. The freeze-drying of the filtrate was carried out to obtain soluble matter, and the insoluble matter was calculated by subtraction, therefore extracts were separated into soluble and insoluble matter by distilled water.

Results and discussion

Changes in weight of the treated sugi sapwood and extracts from sugi sapwood

Weight change of sugi wood treated with aqueous solution of acetic acid and extracts from sugi sapwood was lighter, and it decreased with the increment of concentration of aqueous solution of acetic acid because of elution (Sasaki A. 1997) of extractives and hydrolyzed non-crystalline hemicelluloses of sugi sapwood (see Table 1).

Weight loss of the treated sugi sapwood was about equal to total yield of extracts from sugi sapwood by treatment, within experimental error. Yield of soluble matter of extracts had no change, being around 1%, but insoluble matter increased with the increase of aqueous solution concentration of acetic acid. It can be considered that the inorganic matter in sugi sapwood was extracted or the change of lignin (Dietrich F. 1984) in sugi sapwood was occurred with the increase of aqueous solution concentration of acetic acid.

Table 1. Change in weight of the treated sugi-sapwood and extracts from sugi sapwood

Untreated samples /g	Treatment	Treated samples		Extracts				
		Weight /g	Loss /%	Soluble		Insoluble		Total yield /%
				Weight /g	Yield /%	Weight /g	Yield /%	
30.00	H_2O	29.69	1.03	0.28	0.93	0.00	0.00	0.93
30.00	3 % AcOH	29.64	1.20	0.32	1.07	0.06	0.20	1.27
29.99	30 % AcOH	29.40	1.97	0.30	1.00	0.27	0.90	1.90

FT-IR analyses of the treated sugi sapwood and extracts from sugi sapwood

Because major chemical components in sugi sapwood, such as cellulose, hemicelluloses and lignin, are high organic polymers, the chemical bonds in those compounds can be identified easily by FT-IR spectra (Wang 1991). FT-IR spectra of untreated and treated samples were shown in Fig. 1. The function groups of each absorption band were shown in Table 2. Although OH stretching vibration is located at the wavenumber near 3 400 cm^{-1} and CH stretching vibration is located at the wavenumber near 2 920 cm^{-1}, both are absorption bands based on cellulose, hemicelluloses and lignin. Overlapping in these OH stretching band may beattributed to the presence of hydroxyl groups, and hence it is not easy to discuss these components separately. For the analyses of wood components, several special absorption bands of IR spectra were used. Characteristic absorption bands of lignin were at 1 600 $cm^{-1}$and 1 510 cm^{-1}. The band at 1 260 cm^{-1} was C-O-C stretching vibration of lignin. The band near 1 420 cm^{-1} was primarily due to CH_2 scissor motion in cellulose. The band at 1 160 cm^{-1} corresponds to a glucopyranose ring.

FT-IR spectroscopic analyses of sugi sapwoods treated with aqueous solution of acetic acid indicated that the absorption intensities of OH stretching vibration at 3 400 cm^{-1} and C=C stretching vibration at 1 510 cm^{-1} of benzene ring in lignin had a increasing tendency. This suggested that hydrolysis of hemicelluloses in sugi sapwood increased OH band, and the relative amount of lignin was increased because of elution (Sasaki A. 1997) of extractives and hydrolyzed hemicellulose after sugi sapwood was treated with acetic acid aqueous solution.

FT-IR spectra of extracts from sugi sapwood by treatment with aqueous solution of acetic acid are given in Fig. 2. Absorption intensity of OH stretching vibration at3 400 cm^{-1} in (b) or (c) was less than that in (a) due to inorganic matter extracted from sugi sapwood by 3% or 30% acetic acid

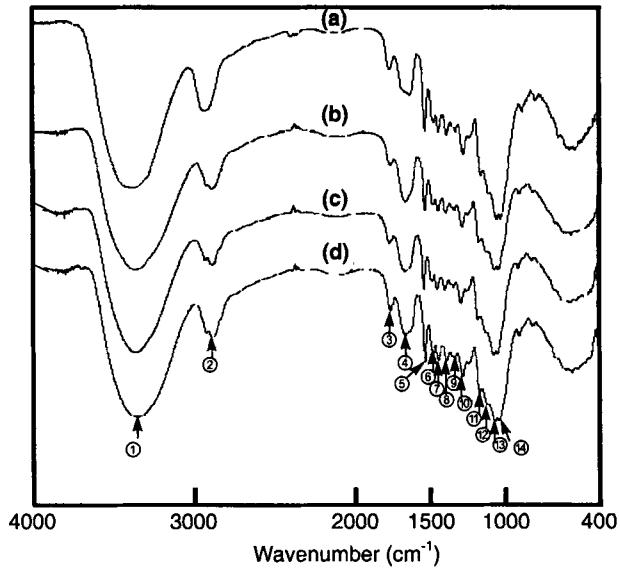

Fig. 1 FT-IR spectra of sugi sapwood treated with aqueous solution of acetic acid.
(a) Untreated, (b) Distilled water, (c) 3% AcOH, (d) 30% AcOH.

solution aqueous and the relative amount of organic matter in extracts was decreased. Absorption intensities of CH_2 stretching vibration at 1 460 cm^{-1} and C-O stretching vibration at 1 020 cm^{-1} of sugar in extracts were increased with the increase of aqueous solution concentration of acetic acid, and absorption of carbonyl group (C=O) stretching vibration at 1 730 cm^{-1} was disappeared because hydrolyses of sugar in extracts were occurred. According to Fig.2, dissolution of lignin in sugi sapwood was not occurred during the treatment with distilled water and 3 % acetic acid

solution aqueous, but the dissolution of lignin was observed during the treatment with 30 % acetic acid solution aqueous judged by the increase of absorption intensities of C=C stretching vibration at 1 510 cm^{-1} of benzene ring in lignin and C-O-C symmetric stretching vibration at 1 280 cm^{-1} of lignin in extracts.

Table 2 Function groups of band assignments in FT-IR spectra of sugi sapwood

Symbols	cm^{-1}	Assignments
①	3400	OH stretching vibrations
②	2860	CH stretching vibrations
③	1760	Carbonyl stretching vibrations of carboxylic acid and esters
④	1600-1660	C=C stretching vibrations of benzene ring in lignin
⑤	1510	C=C stretching vibrations of benzene ring in lignin
⑥	1460	CH_2 symmetric stretching vibrations and OH in-plane bending
⑦	1420	CH_2 scissor vibrations in cellulose, CH in-plane and deformation and aromatic ring stretching vibrations in lignin.
	1380	CH bending vibrations in cellulose and hemicelluloses.
⑧	1280	C-O-C symmetric stretching vibrations in lignin
⑨	1220	C-O-C stretching vibrations of acetyl and carboxyl groups in xylan, and C-O stretching vibrations in lignin
⑩	1160	Glucopyranose ring vibrations or C-O stretching vibrations or O-H bending vibrations in cellulose and hemicelluloses.
⑪	1110	Assiociation band involving C-O stretching or OH bending vibrations in cellulose and hemicelluloses.
	1060	C-O stretching vibrations in cellulose and hemicelluloses.
⑫	1020	C-O stretching vibrations in cellulose and hemicelluloses.
⑬		
⑭		

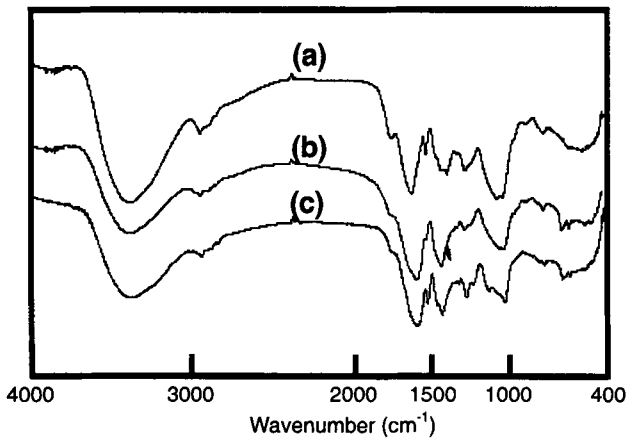

Fig. 2 FT-IR spectra of extracts from sugi sapwood by aqueous solution of acetic acid.
(a) Distilled water, (b) 3% AcOH, (c) 30% AcOH.

Conclusions

Sugi sapwood treated with aqueous solution of acetic acid was lighter than the control in weight, and loss of weight was increased with the increase of acetic acid aqueous solution concentration.

From FT-IR spectra of the treated sugi sapwood and extracts, hydrolyses of hemicelluloses and dissolution of lignin in sugi sapwood were clearly observed.

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